

The University of Chicago

FURTHER STUDIES ON THE
MOLECULAR REARRANGEMENT OF
 β , β -DIPHENYL- β -HYDROXY-
ETHYLAMINE

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1933

By
GORDON HAMILTON STILLSON

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CHAPTER I

INTRODUCTION

A series of investigations have been carried out in this laboratory, under the direction of Professor Stieglitz, on molecular rearrangements which have led from acetophenone oxime, $\text{CH}_3\text{C}(:\text{NOH})\text{C}_6\text{H}_5$, under the influence of phenylmagnesium bromide, to β, β -diphenyl- β -hydroxyethylamine, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{CH}_2\text{NH}_2$, and from this, in turn, by the action of alkali, back to methylimino-benzophenone, $(\text{C}_6\text{H}_5)_2\text{C}:\text{NCH}_3$. The present investigation was undertaken in an effort to shed further light on the mechanism of these interesting molecular rearrangements.

The results of the previous workers will first be reviewed briefly, in order to establish the basis for the present studies.

Miss Maver,¹ in studying the action of Grignard reagents on acetophenone oxime, $\text{CH}_3\text{C}(:\text{NOH})\text{C}_6\text{H}_5$, reported that a highly concentrated ether solution of phenylmagnesium bromide reacts with the oxime to form, by an addition reaction, methyldiphenylmethyl-hydroxylamine, $\text{CH}_3(\text{C}_6\text{H}_5)_2\text{C}^2\text{NHOH}$.

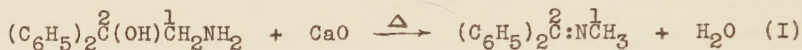
Cole² later showed that the product of the above reaction is not a derivative of hydroxylamine, but, as the result of a molecular rearrangement, an alkamine, β, β -diphenyl- β -hydroxyethylamine, $(\text{C}_6\text{H}_5)_2\text{C}^2(\text{OH})\text{CH}_2^1\text{NH}_2$. In this rearrangement the nitrogen radical evidently migrates from the ketonic carbon atom (2) to carbon atom (1) of the methyl group. The structure of the

¹Mary E. Maver, Doctorate Dissertation, University of Chicago, 1926. Abstracts of Theses, Science Series, IV, 111 (1926).

²John E. Cole, Doctorate Dissertation, University of Chicago, 1929. Abstracts of Theses, Science Series, VII, 145 (1929).

alkamine was proven by Cole by its synthesis from glycine ester, $C_2H_5O.C(:O)CH_2NH_2$, and phenylmagnesium bromide.

Maver,¹ Cole,² and Lenth,³ the latter in continuing the investigations, found that the alkamine itself, when heated with soda-lime, or calcium oxide, undergoes a molecular rearrangement, and with the loss of a molecule of water, forms methyliminobenzophenone, $(C_6H_5)_2C:NCH_3$.



It is clear that in this rearrangement, the nitrogen atom, carrying with it the methyl group, goes back to its original combination with carbon atom (2), a ketonic structure being formed again.

The purpose of Lenth's work was to determine, if possible, the mechanism of the last rearrangement reaction. Two theories were considered:

- (1) That benzophenone and methylamine are formed as the result of a thermal decomposition of the alkamine, and then reunite to give the ketimine.
- (2) That the rearrangement takes place through the formation of an intermediate compound.

The first theory was tested by the slow addition of soda-lime to a molten mixture of benzophenone and methylammonium chloride. Methyliminobenzophenone was formed in this reaction, but the yield was only about 4 per cent of the theoretical. Since the yield of the product from the rearrangement of the alkamine is of the order of 80 per cent, this mechanism does not account

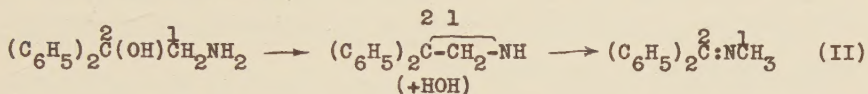
¹Loc. cit.

²Loc. cit.

³C. W. Lenth, Doctorate Dissertation, University of Chicago, 1930. Abstracts of Theses, Science Series, VIII, 101 (1930).

for the principal reaction, although it might contribute to it.

In the second theory, the intermediate compound is considered to be unsymmetrical diphenylethylenimide, $(C_6H_5)_2\overline{C-CH_2-NH}$. The following equation expresses the course of the reaction according to this theory:



The ring compound is a derivative of ethylenimide, $\overline{CH_2-CH_2-NH}$, the structure of which was determined by Marckwald and Howard.¹ Efforts to prepare unsymmetrical diphenylethylenimide have thus far failed,² although it is our present opinion that such a preparation is not impossible. Other cyclic bases have been isolated successfully.³ If a halogen atom could be substituted for the hydroxyl group of the alkamine, and the hydrogen halide eliminated between that carbon atom and the amino group, the desired ring structure would result. Emde⁴ succeeded in substituting chlorine and bromine for the hydroxyl group in ephedrine, an amino alcohol, $(C_6H_5).CHOH.CHCH_3.NHCH_3$, of a structure somewhat similar to ours. If a like substitution could be effected in the alkamine under investigation, it should be a simple matter to remove the hydrogen chloride or bromide with sodamide in anhydrous liquid ammonia solution. This point is mentioned merely as a suggestion to future workers.

Lenth proceeded to study possible ring formation and rearrangement of the monomethyl derivative of the alkamine,

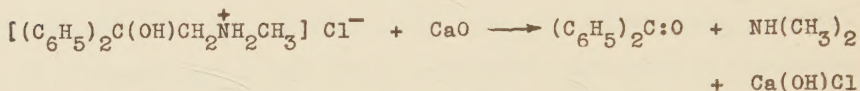
¹Marckwald and Howard, Ber. 32, 368, (1899).

²Lenth, loc. cit.

³Neber and Burgard, Ann. 493, 281, (1932); Darapsky and Spannagel, J. prakt. Chem., 92, 272, (1915); Weiszberger and Bach, Ber. 64, 1105, (1931). For a review of the literature see: Hollins, C., "Synthesis of Nitrogen Rings," (London, Ernest Benn, Ltd.), pp. 2-21.

⁴Emde, Helv. Chim. Act. 12, 384, (1929).

$(C_6H_5)_2C(OH)CH_2NHCH_3$. Cole had prepared and analyzed this methyl compound, and had named it β, β -diphenyl- β -hydroxyethylmethylamine. Lenth heated the hydrochloride of the methylated alkamine with calcium oxide, duplicating the experimental conditions under which the heating of the unmethylated alkamine was carried out. and obtained a quantitative yield of benzophenone and dimethylamine, according to the equation:



However, when he heated the benzoyl derivative, β, β -diphenyl- β -hydroxyethylmethylbenzamide, $(C_6H_5)_2C(OH)CH_2N(CH_3).C:O.C_6H_5$, with calcium oxide, at $300^\circ C.$, he obtained a yellow oil, which boiled at $112^\circ C./4mm.$. The oil was a base, and analyses of its chloroplatinate and hydrochloride, and its behavior on hydrolysis, indicated that it was unsymmetrical diphenylethylenemethylimide, $(C_6H_5)_2C\overline{-CH_2-NCH_3}$. This is seen to be the N-methyl derivative of the supposed intermediate of the alkamine rearrangement. Since this triatomic ring derivative was obtained from the methylated alkamine through a reaction analogous to that leading to the molecular rearrangement of the original alkamine, its formation was thought to be substantial evidence that the primary amino alcohol follows a similar course in its transformation to methylimino-benzophenone, as expressed in equation (II), page 3.

It was the original purpose of the present author to attempt to isolate the unmethylated ring compound, $(C_6H_5)_2C\overline{-CH_2-NH}$, by treatment of the benzoyl derivative of the unmethylated alkamine with alkali, following Lenth's methods with the methyl derivative. It seemed advisable, however, to repeat some of the work of Lenth, not only as a check on it, but as a more thorough

study of the reactions and compounds involved. This part of the work of Lenth was carried out at the very end of his investigations. In the present study many unforeseen complications and irregularities developed, which caused the preparation and study of the methylated ring derivative to become the main objective of this dissertation. It seemed more important to smooth out the pioneering work of Lenth, than to go on, leaving a sketchy background. In so doing, many useful and interesting corrections, facts, and laboratory details were uncovered.

II. DISCUSSION OF RESULTS

1. Preparation of the N-Benzoyl Derivative of

β, β -Diphenyl- β -hydroxyethylmethylamine, $(C_6H_5)_2C(OH)CH_2N(CH_3)COC_6H_5$
by the Methods of Cole and Lenth.

It was found possible to duplicate completely the preparation of β, β -diphenyl- β -hydroxyethylmethyl ammonium chloride, $[(C_6H_5)_2C(OH)CH_2NH_2^+(CH_3)] Cl^-$, of the melting point 215° , by the methods of Cole and Lenth. However, on benzylation of this product, in pyridine or aqueous solution by the Schotten-Baumann method, the benzoyl derivative of melting point 177° , described by Lenth, was never obtained in a pure condition. Repeated recrystallization always gave a product melting at 183° ; but this is the melting point of the unmethylated β, β -diphenyl- β -hydroxyethylbenzamide, $(C_6H_5)_2C(OH)CH_2NH.COC_6H_5$, as reported by Cole, Lenth, and Bettzieche.¹

Recourse was taken then to the preparation of the benzene-sulfonamides of the two alkamines, with a view, first, to their effectual separation with the aid of the Hinsberg method,² and,

¹Z. Physiol. Chem. 140, 244 (1924).

²Ber. 38, 906 (1905).

second, to the possible substitution of the sulfonamides for the benzamides in the study of the molecular rearrangement with lime.

2. Preparation of the Benzenesulfonyl Derivatives of the Methylated and Unmethylated Alkamines, and their Separation by a Modified Hinsberg Method.

According to Hinsberg,¹ as is well known, the benzene-sulfonyl derivatives of primary amines are more or less soluble in aqueous alkali solutions, while those of secondary amines are not. With this in view, samples of the N-benzenesulfonate of the unmethylated alamine were prepared and analyzed. The compound, β, β -diphenyl- β -hydroxyethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2NH.SO_2C_6H_5$, is but sparingly soluble in aqueous sodium or potassium hydroxides. Mixtures of this unmethylated sulfonamide and the methylated sulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$, were prepared from a mixture of the primary and secondary alamine hydrochlorides obtained from the incomplete liquid ammonia methylation described by Cole. The mixed sulfonamides were slowly leached out with aqueous (12 per cent) potassium hydroxide. Although the extract, on acidification, was found to contain the sulfonamide of the unmethylated alamine, the residue, insoluble in alkali, never reached a constant melting point.

It was then discovered that the two sulfonamides are easily soluble in 10 per cent alcoholic potassium hydroxide. Subsequent addition of water precipitates, by dilution of the alcohol, the methylated sulfonamide. After a repetition of the process a product is obtained whose melting point cannot be changed by further recrystallization. As shown by analysis, it is pure β, β -diphenyl- β -hydroxyethylmethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$.

¹Loc. cit.

3. Heating of β, β -Diphenyl- β -hydroxyethylmethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$, an Attempt to Obtain the Ring Compound of Lenth, $(C_6H_5)_2C-CH_2-NCH_3$.

The methylated sulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$, was heated at length with lime at 300° , as Lenth heated the benzoyl derivative. The product is unsymmetrical diphenylethane, $(C_6H_5)_2CH.CH_3$. The reaction, evidently of a complex character but involving no rearrangement, was not investigated further.

4. A New Method for the Preparation of Pure β, β -Diphenyl- β -hydroxyethylmethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$.

Upon allowing a hot, alcoholic potassium hydroxide (10 per cent) solution of the pure benzenesulfonyl derivative of the non-methylated alkamine to cool, its potassium salt, $(C_6H_5)_2C(OH)CH_2NKSO_2C_6H_5$, crystallizes out. Treatment of an aqueous solution of this potassium salt with dimethylsulfate causes the precipitation of the sulfonamide of the methylated alkamine, $(C_6H_5)_2COH.CH_2N(CH_3)SO_2C_6H_5$. Recrystallization from alcoholic potassium hydroxide gives a very pure product in good yield.

5. Recovery of Pure Amines from Their Benzenesulfonyl and Benzoyl Derivatives, by a New Method.

There are two standard methods for removing acyl groups from amines. By Hinsberg's method¹ acid amides are heated in sealed tubes with concentrated hydrochloric acid at 160° . The other method² requires heating of the amides in an open vessel with concentrated sulfuric acid at 130° . Either method causes this type of alkamine to decompose. Cole describes the result of heating these compounds with concentrated acids.

An attempt was made to methylate the benzoyl derivative

¹Ber. 38, 906 (1905).

²Cocker and Lapworth, J. Chem. Soc., Aug. 1931, p. 1894.

An attempt was made to methylate the benzoyl derivative of the unmethylated alkamine, $(C_6H_5)_2C(OH)CH_2NHCOC_6H_5$, by the method which Cole used for the methylation of the primary alkamine itself. In this method a sodium-amido salt of the structure, $(C_6H_5)_2C(OH)CH_2N(H)Na$, is first formed by the addition of metallic sodium to a liquid ammonia solution of the alkamine. Subsequent treatment of this salt with methyl iodide causes a methyl group to be substituted for the sodium atom. If an acyl derivative of the alkamine could be made to react in the same manner, the formation of a tertiary amino group could be prevented. However, when the benzoyl derivative is used, the reaction results in a mixture of the primary, secondary, and tertiary free amines. It is evident that the acyl group is saponified away. This suggested a very efficient method for removing benzoyl groups from alkamines, since it is simple and almost complete, and is carried on at low temperatures.

The method was immediately applied to the benzenesulfonyl derivatives of both the non-methylated and methylated alkamines, and to the benzamide of the methylated alkamine. The acyl groups are successfully removed in all cases. For further orientation, benzenesulfonanilide, $C_6H_5SO_2.NHC_6H_5$, and benzenesulfonmethyl-anilide, $C_6H_5SO_2.N(CH_3)C_6H_5$, were subjected to the same treatment as the acyl derivatives of the alkamines, and the acid groups are found to be removed smoothly in an analogous fashion.

Thus, a way was found at last, for preparing the pure compound, β, β -diphenyl- β -hydroxyethylmethylbenzamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)COC_6H_5$, free of the non-methylated derivative, which is desired for the production of the ring compound, unsymmetrical diphenylethylenemethylimide, $(C_6H_5)_2C-CH_2-NCH_3$, prepared by Lenth in impure form. Since by modifying Hinsberg's method of

separation and incorporating the methylation into it, it is now possible to produce β, β -diphenyl- β -hydroxyethylmethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$, of the highest purity, it is now a simple matter to prepare also the free base, β, β -diphenyl- β -hydroxyethylmethylamine, $(C_6H_5)_2C(OH)CH_2NHCH_3$, of a purity far exceeding that attained by previous methods.

6. Preparation of Pure β, β -Diphenyl- β -hydroxyethylmethylammonium Chloride, $[(C_6H_5)_2C(OH)CH_2\overset{+}{N}(CH_3)_2] Cl^-$, from β, β -Diphenyl- β -hydroxyethylmethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$.

By the method described the benzenesulfonyl group was removed from a pure sample of β, β -diphenyl- β -hydroxyethylmethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$. The compound which results is pure β, β -diphenyl- β -hydroxyethylmethylamine, $(C_6H_5)_2C(OH)CH_2NHCH_3$, a compound prepared and described by Cole, but never before obtained in the pure state by the present writer. The hydrochloride of this alkamine, β, β -diphenyl- β -hydroxyethylmethylammonium chloride, $[(C_6H_5)_2C(OH)CH_2\overset{+}{N}(CH_3)_2] Cl^-$, varies somewhat, in melting point, from that prepared by Cole.¹ It is our present opinion that Cole's hydrochloride also contained some of the dimethylated salt, β, β -diphenyl- β -hydroxyethyldimethylammonium chloride, $[(C_6H_5)_2C(OH)CH_2\overset{+}{N}(CH_3)_2H] Cl^-$.

The hydrochloride of the mono-methylated alkamine, β, β -diphenyl- β -hydroxyethylmethylammonium chloride, $[(C_6H_5)_2C(OH)CH_2\overset{+}{N}(CH_3)_2] Cl^-$, was converted into the benzoyl derivative by the Schotten-Baumann method. A compound is obtained which melts at $159-60^\circ$, which does not compare very favorably with Lenth's 177° for the same compound. This total disagreement in melting points would have been discouraging but for the results of

¹See "Experimental Results," page 20.

an experiment performed earlier in the work. When the methods of Cole and Lenth failed to give the desired mono-methylated salt, β, β -diphenyl- β -hydroxyethylmethylammonium chloride, $[(C_6H_5)_2C(OH)CH_2N^+(CH_3)H_2] Cl^-$, in a pure state, the present author decided to prepare it from sarcosine ethyl ester, $C_2H_5O_2C.CH_2NHCH_3$, by treatment with phenylmagnesium bromide. Lenth had used this method of preparation, on a very small scale, to prove the structure of the mono-methylated alkamine, $(C_6H_5)_2C(OH)CH_2NHCH_3$. The hydrochloride obtained from this Grignard reaction was converted into a benzoyl derivative which melts at 159° , and which does not depress the melting point of the benzamide prepared by the later method. When the benzoyl group is removed with the aid of sodium in liquid ammonia, an amine results whose benzenesulfonyl derivative proves to be β, β -diphenyl- β -hydroxyethylmethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$. Analysis shows the benzoyl derivative to have a composition corresponding to $C_{22}H_{21}NO_2$, the empirical formula for β, β -diphenyl- β -hydroxyethylmethylbenzamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)COC_6H_5$. In the face of this evidence, obtained from two entirely different, direct methods, it seems certain that the melting point (177°) reported by Lenth for the methylated benzoyl derivative, $(C_6H_5)_2C(OH)CH_2N(CH_3)COC_6H_5$, is erroneous.

7. Heating of β, β -Diphenyl- β -hydroxyethylmethylbenzamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)COC_6H_5$, with Calcium Oxide, to Give Ring Compound, Unsymmetrical Diphenylethylenemethylimide,



When β, β -diphenyl- β -hydroxyethylmethylbenzamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)COC_6H_5$, is heated with calcium oxide, at 275° , a bright yellow oil is obtained. This is shown, by a carbon and hydrogen analysis, and by an analysis of its chloroplatinate,

to have the required composition for unsymmetrical diphenylethylenemethylimide, $(C_6H_5)_2C-CH_2-NCH_3$. Hydrolysis with acid occurs according to the equation:



III. EXPERIMENTAL RESULTS

1. Attempts to Prepare β,β -Diphenyl- β -hydroxyethylmethylbenzamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)COC_6H_5$, by Lenth's Method.

The alkamine, $(C_6H_5)_2C(OH)CH_2NH_2$, is dissolved in anhydrous liquid ammonia (10 g. of alkamine requires about 300 c.c. of ammonia), in a 500 c.c. Dewar flask. The flask cannot be the silvered variety, since that would make it impossible to observe the color changes. Metallic sodium (approximately 1 mole) is introduced, in small cubes, until a permanent blue color is reached. A flocculent, white precipitate consisting of a mixture of the mono- and di-sodium salts settles out. Without filtration one mole of methyl iodide is added to the mixture in the Dewar flask; stirring is effected by a stream of dry ammonia gas. The blue color is discharged immediately. A finer, white precipitate remains. The ammonia is allowed to evaporate overnight, and the residue is extracted with ether and water. The water solution is separated and discarded. The ether solution is dried with anhydrous sodium sulfate and fresh calcium oxide, and filtered without being exposed to the absorption of water. When dry hydrogen chloride is passed into the ether solution, a white precipitate is formed almost immediately. This, upon recrystallization from an absolute alcohol solution with anhydrous ether, generally melts somewhere between the rather broad limits of 204° and 220° . Further recrystallizations bring the melting point to 229° , the melting point of the dimethylated salt, β,β -diphenyl- β -hydroxy-

ethyldimethylammonium chloride, $[(C_6H_5)_2C(OH)CH_2NH^+(CH_3)_2] Cl^-$. It is suspected that the product of the first recrystallization is a mixture of the hydrochlorides of the unmethylated, monomethylated, and dimethylated alkamines. This suspicion is confirmed by the preparation and isolation of their benzenesulfonyl derivatives, by methods to be described later. The melting points of these derivatives agree with this belief.

At no time during the research was it possible to prepare a benzoyl derivative of the methylated alkamine melting at 177° from any of the samples of the hydrochloride melting around 215° . The ultimate melting point of the products prepared is 183° , which is the melting point of the unmethylated benzoyl derivative, $(C_6H_5)_2C(OH)CH_2NHCOC_6H_5$. Fractional recrystallization from chloroform and low-boiling ligroin fails to bring out the desired compound. After an exhaustive study of these methods, they were finally abandoned.

2. Preparation and Isolation of the N-Benzenesulfonamides of β,β -Diphenyl- β -hydroxyethylamine, $(C_6H_5)_2C(OH)CH_2NHSO_2C_6H_5$, and of β,β -Diphenyl- β -hydroxyethylmethylaniline, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$.

The unmethylated alkamine (10 g.), $(C_6H_5)_2C(OH)CH_2NH_2$, is suspended in water (250 c.c.) in which solid potassium carbonate (2.5 g.) has been dissolved. Slowly, with stirring, 12.5 g. (1.5 mols) of benzenesulfonyl chloride is added to this mixture. The reaction is kept alkaline with solid potassium carbonate. A white, crystalline solid separates out, generally on the wall of the reaction flask. The mixture is stirred for about a half an hour to assure a complete reaction. The crystals are collected on a filter, washed well with water, and recrystallized from 95 per cent alcohol. This product is pure, melts at 138° , and weighs

about 12 g., which represents a yield of 75 per cent of the theoretical yield.

The solubility of the primary sulfonamide in potassium carbonate solution is negligible, so that it is not necessary to acidify the reaction mixture to precipitate the product.

Bettzieche's method¹ for the preparation of acyl derivatives can also be used for the preparation of the compound, β, β -diphenyl- β -hydroxyethylbenzenesulfonamide, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{CH}_2\text{NH}\cdot\text{SO}_2\text{C}_6\text{H}_5$. In this method the alkamine is dissolved in 50 c.c. of ether, and the resulting solution poured upon 175 c.c. of 15 per cent aqueous sodium hydroxide solution. The acyl chloride (1.5 mols) is then added to the mixture. The ether and the excess of acid chloride are removed by the passing of air through the mixture. By this method of Bettzieche a high-melting compound is sometimes encountered, which has a very fine, silky, needle-like structure. Recrystallized from alcohol, the silky crystals form a compound of the desired melting point, 138°. The high-melting compound, which melts above the range of the sulfuric acid bath (260°), is possibly a condensation product, but has not been investigated further.

Analysis² of β, β -diphenyl- β -hydroxyethylbenzenesulfonamide, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{CH}_2\text{NHSO}_2\text{C}_6\text{H}_5$ (m.p. 138°):

3.414 mg. sample gave 0.125 c.c. of N_2 at 27°C. and 749.8 mm. (corrected).

3.345 mg. sample gave 0.123 c.c. of N_2 at 28°C. and 749.9 mm. (corrected).

Calculated for $\text{C}_{20}\text{H}_{19}\text{NO}_2\text{S}$:

N_2 3.97 per cent

Found:

4.11 per cent
4.11

¹Bettzieche, Z. Physiol. Chem. 140, 244, (1924).

²Micro-analytical methods of Pregl are used in all of the analyses. Cf. "Quantitative Organic Microanalysis" Blackiston's Son & Co.

Mixtures of the methylated and unmethylated alkamines, as obtained from the liquid ammonia methylation of the alkamines, are converted into the sulfonamides, and give mixtures of the derivatives melting, sluggishly, around 120°. These mixed sulfonamides were washed repeatedly on a filter with an aqueous 12 per cent solution of potassium hydroxide in an effort to leach out the alkali-soluble component. Although the extract, on being acidified with dilute hydrochloric acid, is found to contain the benzenesulfonyl derivative of the primary amine alcohol, $(C_6H_5)_2C(OH)CH_2NHSO_2C_6H_5$, of the melting point 138°, it has never been possible to obtain a compound of constant melting point from the alkali insoluble residue. Shaking of the mixture of the two sulfonamides with alkali gives the same result.

The non-methylated and the monomethylated benzenesulfonamides have been separated finally with the aid of alcoholic potassium hydroxide. A one gram sample of the mixture of the two is dissolved in 40 c.c. of 95 per cent alcohol. To this solution 40 c.c. of 10 per cent alcoholic potassium hydroxide solution (10 g. of alkali in 100 c.c. of 95 per cent alcohol) is added. Dilution with twice the volume of water causes the precipitation of white crystals melting at 129° after a further recrystallization from pure 95 per cent alcohol. The behavior of the compound upon melting indicates impurity. Another recrystallization, but this time from the 10 per cent alcoholic alkali, gives a product melting at 144°. Further recrystallization from either the alkali or 95 per cent alcohol does not change this melting point, which is quite sharp. The filtrates from the alkali recrystallizations, upon being acidified with dilute hydrochloric acid, give crystals melting at 138°, which do not depress the melting point of known β, β -diphenyl- β -hydroxyethylbenzenesulfonamide,

$(C_6H_5)_2C(OH)CH_2NHSO_2C_6H_5$. The compound melting at 144° shows the following analysis, agreeing with the formula for β,β -diphenyl- β -hydroxyethylmethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$:

3.815 mg. of sample gives 1.976 mg. of H_2O , and
9.629 mg. of CO_2 .

3.842 mg. of sample gives 0.145 c.c. of N_2 at $29^\circ C.$ and
745.8 mm. (corrected).

Calculated for $C_{21}H_{21}NO_3S$:

Found:

H:	5.76 per cent	5.80 per cent
C:	68.62	68.84
N:	3.82	4.18

Later the above procedure was varied somewhat. To the warm alcoholic solution of the mixture of sulfonamides is added an excess of aqueous 50 per cent potassium hydroxide solution (50 g. of KOH in 50 c.c. of water). This change in procedure saves the time necessary to dissolve the solid alkali in 95 per cent alcohol.

3. Preparation of β,β -Diphenyl- β -hydroxyethylmethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$, by Direct Methylation of β,β -Diphenyl- β -hydroxyethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2NH.SO_2C_6H_5$, by the Use of Dimethyl Sulfate.

β,β -Diphenyl- β -hydroxyethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2NH.SO_2C_6H_5$, (12 g.) is dissolved in 200-250 c.c. of 95 per cent alcohol, heated almost to boiling. To this solution is added 4 g. of potassium hydroxide dissolved in a minimum of water. The solutions must be kept hot to avoid the precipitation of the potassium salt of the sulfonamide. The volume of the solution is increased to 500 c.c. by dilution with water. The alkali salt now will not precipitate. Redistilled dimethyl sulfate (15 to 18 c.c.) is now introduced, in three portions, with stirring. Crystals of the methylated sulfonamide separate almost immediately, with the evolution of considerable heat. These are

collected on a filter, and recrystallized by precipitation with water from an alcoholic potassium hydroxide solution. The melting point is 144° for the resulting crystals. The alkaline filtrates are combined, and the unchanged primary sulfonamide precipitated with dilute hydrochloric acid, to be used again.

The potassium salt of the sulfonamide, mentioned above, can be isolated; recrystallized from 95 per cent alcohol, it is found to melt at 231° . It shows the following analysis for potassium, agreeing with the formula, $(C_6H_5)_2C(OH)CH_2NKS O_2C_6H_5$:

5.125 mg. of sample gives 1.224 mg. of K_2SO_4 .
4.669 mg. " " " 1.098 mg. " " "

Calculated for $C_{20}H_{18}NO_3SK$:

Found:

K: 10.00 per cent 10.55, 10.72 per cent

4. Attempt to Methylate β,β -Diphenyl- β -hydroxyethylbenzamide, $(C_6H_5)_2C(OH)CH_2NH.COC_6H_5$, in Liquid Ammonia, Leading to the Discovery of a New Method for the Removal of Acyl Groups from Acylated Amines.

β,β -Diphenyl- β -hydroxyethylbenzamide (2 g.), $(C_6H_5)_2C(OH)CH_2NH.COC_6H_5$, is added to 250 c.c. of anhydrous liquid ammonia, which does not completely dissolve the amide. As one mole of metallic sodium, cut into pea-sized cubes, is added, the compound gradually dissolves, and the solution turns yellow. The reaction mixture is stirred constantly with dry gaseous ammonia from a small tank, by means of a bubbling tube extending to the bottom of the Dewar flask. When the last of the crystals is dissolved, the solution becomes cloudy, and then turns bluish-green in color. Stirring is continued for five minutes to insure consumption of the sodium. Gaseous methyl bromide is then passed into the mixture for five minutes. During this time, the color of the solution changes from blue to green, brown, and yellow, and finally the solution becomes colorless. The ammonia is evaporated,

and the residue is extracted with ether and water. The ether solution is freed of ether, the oily residue is dried over phosphorus pentoxide, and then redissolved in anhydrous ether. The introduction of dry hydrogen chloride causes the precipitation of a white, crystalline product. This is recrystallized by precipitation, with dry ether, from an absolute alcohol solution. The first crystals thus precipitated melt at 195° , and do not depress the melting point of β, β -diphenyl- β -hydroxyethylammonium chloride, $[(C_6H_5)_2C(OH)CH_2\overset{+}{N}H_3] Cl^{-}$, M.P. 195° . The next fraction of crystals melts at 205° , a typical melting point for mixtures of the hydrochlorides of the monomethylated and non-methylated alkamines. Evidently the benzoyl group is removed from the amide by the action of sodium amide.

Although the above procedure is not successful as a methylation, it provides a new method, hitherto unrecorded in the literature, for the removal of an acyl group from an acyl amide. Analogous reactions were carried out on other compounds, in order to test the general character of the reaction.

The unmethylated benzenesulfonyl derivative (5 g.), $(C_6H_5)_2C(OH)CH_2NHSO_2C_6H_5$, is dissolved in liquid ammonia (250 c.c.), and small cubes of metallic sodium are added until the permanent blue color of sodium-ammonia solutions results. The ammonia is evaporated, and the residue is extracted with ether and water. Upon evaporation, the ether layer gives crystals which melt at 110° , the melting point of pure β, β -diphenyl- β -hydroxyethylamine.¹ The hydrochloride of these crystals is formed and melts at 195° . It does not depress the melting point of known β, β -diphenyl- β -hydroxyethylammonium chloride, $[(C_6H_5)_2C(OH)CH_2\overset{+}{N}H_3] Cl^{-}$ (195°).

¹Maver, Cole, Lenth, Loc. cit.; Weidenkaff, Ber. 38, 1687, (1905); Bettzieche, Z. Physiol. Chem. 140, 244 (1924).

Benzenesulfonanilide, $C_6H_5SO_2.NHC_6H_5$, m.p. 112° , was prepared and subjected to the process. The compound (2.5 g.) was dissolved in 100 c.c. of liquid ammonia, and 2 mols of metallic sodium were added to the solution. After evaporation of the ammonia and extraction with ether and water, evaporation of the ether layer left a brown oil which had the odor of aniline. The hydrochloride of this oil melts at 196° , and does not depress the melting point of known aniline hydrochloride (m.p. 195°).

Benzenesulfonmethylanilide, $C_6H_5SO_2.N(CH_3)C_6H_5$, m.p. 80° , was prepared, and a 2.5 gram sample was treated in the same way. The reaction gives a hydrochloride of the melting point $121-2^\circ$, that of methylaniline hydrochloride. The oil itself boils at $191-2^\circ$, the boiling point of methylaniline.

5. Preparation of β, β -Diphenyl- β -hydroxyethylmethylammonium Chloride, $[(C_6H_5)_2C(OH)CH_2\overset{+}{N}(CH_3)_2] Cl^-$, from its Benzenesulfonyl Derivative, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$.

β, β -Diphenyl- β -hydroxyethylmethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$ (2.2 g.), is dissolved in 150 c.c. of liquid ammonia, and treated with metallic sodium (2 mols) to a permanent blue color. After the ammonia has evaporated, the residue is extracted with ether and water. The ether solution is then extracted with dilute hydrochloric acid, which leaves in the ether any of the sulfonamide which has not reacted with the sodium. The acid solution is made alkaline with solid potassium carbonate, which precipitates the free base, β, β -diphenyl- β -hydroxyethylmethylamine, $(C_6H_5)_2C(OH)CH_2NHCH_3$, m.p. 90° . Cole reported 90° as the melting point of this compound. Its benzenesulfonyl derivative melts at 144° , the melting point of the known methylated derivative.

The hydrochloride of the alkamine, β, β -diphenyl- β -

hydroxyethylmethylanmonium chloride, $[(C_6H_5)_2C(OH)CH_2\overset{+}{N}(CH_3)H_2]Cl^-$, is found to melt at 209° , decomposing at 215° . Cole reported 215° , with decomposition. Cole's chloride, however, was not made from the purified free base, but from the ether extract of the liquid ammonia methylation of β, β -diphenyl- β -hydroxyethylamine, $(C_6H_5)_2C(OH)CH_2NH_2$. This extract has been found by the present author to contain not only the monomethylated alkamine, but the non-methylated and dimethylated as well. Some of the supposed monomethylated hydrochloride prepared by the author, using Cole's method, is found to melt first at 215° , and then, upon many recrystallizations, at 229° , the melting point of the dimethylated salt. It is characteristic of most of these compounds that a mixture of an analogous pair of primary and secondary alkamine derivatives melts, not below the melting point of either, but at some point between their respective melting points. In analogous derivatives, there is never a separation of more than ten degrees between the melting points of the methylated and non-methylated compounds. It is quite possible that Cole, in recrystallizing impure mixtures of the primary, secondary, and tertiary alkamine hydrochlorides, reached a composition of monomethylated and dimethylated salts which crystallized from solvents in a constant proportion, such that the melting point lay between those of the individual compounds. When this equilibrium is disturbed by fractional crystallization, the higher melting point is reached.

6. Preparation and Analysis of β, β -Diphenyl- β -hydroxyethylmethylbenzamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)COC_6H_5$.

The benzenesulfonamide of the methylated alkamine (10 g.), $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$, is treated with liquid ammonia and sodium as described in Section 5. When the free base is precipitated from the acid solution with potassium carbonate, the mixture

is extracted with ether and poured into 200 c.c. of water. Benzoyl chloride (6 g.) is then added slowly, with stirring, to the ether-water mixture. The derivative separates out as a mobile, gummy mass at the intersurface between the ether and water layers. When the ether and the excess of the acid chloride are removed by the passing of air through the mixture, the product becomes crystalline. Upon being recrystallized once from 95 per cent alcohol, the compound melts at $159-60^{\circ}$. This derivative does not depress the melting point of the benzoyl derivative of the amine prepared from sarcosine ethylester, to be described shortly. The yield of the pure product is 8 g. (88 per cent).

Analysis (Pregl) for carbon and hydrogen:

2.746 mg. sample gives 1.531 mg. of H_2O .
 2.746 mg. " " 8.039 mg. of CO_2 .
 3.077 mg. sample gives 1.732 mg. of H_2O .
 3.077 mg. " " 9.005 mg. of CO_2 .

Calculated for $C_{22}H_{21}O_2N$:

Found:

H: 6.39 per cent	6.24, 6.30 per cent
C: 79.78	79.84, 79.81

7. Preparation of β, β -Diphenyl- β -hydroxyethylmethylammonium Chloride, $[(C_6H_5)_2C(OH)CH_2\overset{+}{N}(CH_3)H_2] Cl^-$, by the Action of Phenylmagnesium Bromide on Sarcosine Ethylester Hydrochloride, $[O:C(OC_2H_5)CH_2\overset{+}{N}(CH_3)H_2] Cl^-$, and the Formation of the Benzoyl Derivative, $(C_6H_5)_2C(OH)CH_2N(CH_3)COC_6H_5$.

Sarcosine ethylester hydrochloride is prepared, in good yield, by the method of Staudt.¹ The preparation is expensive, and rather laborious. Phenylmagnesium bromide is prepared from 21 g. of magnesium, 150 g. of phenylbromide, and 450 c.c. of anhydrous ether. To this reagent is added 15 g. of sarcosine ester hydrochloride. The reaction mixture is decomposed by hydrochloric

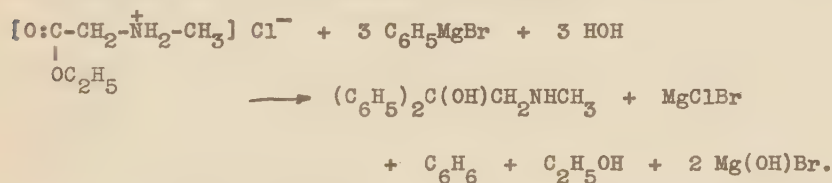
¹Staudt, Z. Physiol. Chem. 146, 286 (1925).

acid and ice, and extracted repeatedly with ether; the ether solution is discarded. The aqueous solution is made alkaline with ammonium hydroxide, which causes the precipitation of a flocculent precipitate. This is removed by ether. The ether solution is dried with anhydrous sodium sulfate and calcium oxide. Treatment of the anhydrous solution with hydrogen chloride causes the precipitation of a hydrochloride, which, recrystallized, melts at 210°.

Comparison of melting points:

	<u>This compound:</u>	<u>$[(C_6H_5)_2C(OH)CH_2\overset{+}{N}(CH_3)H_2] Cl^-$:</u>
	210°	209°
Ficrate-	182°	182° (Lenth)
Benzenesulfonamide-	143°	144°

This evidence indicates that the product from the Grignard reaction is β, β -diphenyl- β -hydroxyethylmethyllummonium chloride. The reaction can be represented as follows:



This reaction gives a yield of 12.2 g. (48 per cent) of the crude alkamine hydrochloride.

Some of this compound (5 g.) is treated with benzoyl chloride (2.7 g.) and potassium carbonate (2 g.) in 100 c.c. of water, with stirring. The product from this reaction, recrystallized from 95 per cent alcohol, melts at 159°, and does not depress the melting point of the methylated alkamine benzamide, as prepared by the other method. The structure of the benzoyl derivative is now established as: $(C_6H_5)_2C(OH)CH_2N(CH_3)-COC_6H_5$, m.p. 159°.

8. The Thermal Decomposition of β, β -Diphenyl- β -hydroxy-

ethylmethylbenzamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)COC_6H_5$, to Form Unsymmetrical Diphenylethylenemethylimide, $(C_6H_5)_2C-CH_2-NCH_3$.

The benzoyl derivative of the methylated alkamine (6 g.), m.p. 159° , is intimately mixed with fresh, finely powdered calcium oxide (6 g.). This mixture is placed in a large Pyrex test-tube, which is fitted with a small reflux condenser, and an entry tube for the passage of dry nitrogen. The reaction tube is then immersed in a bath of "600-W," heavy-duty transmission oil. The exit tube from the reflux condenser is connected with a small trap containing dilute hydrochloric acid, in order to absorb any volatile amines which might be given off. The whole system is filled with dry nitrogen, supplied from a tank by slow bubbling through concentrated sulfuric acid. The temperature of the bath is then raised with the aid of a Meker burner. Between 250° and 260° decomposition takes place, as is evident from the greatly increased rate of the bubbles escaping through the acid trap. The temperature is held between 275° and 280° for two hours. Drops of yellow oil can be seen to condense on the nitrogen entry tube and on the lower portion of the condenser. At the end of two hours, the bath is removed, and the contents of the tube are allowed to cool in the nitrogen atmosphere. The residue in the flask is then extracted repeatedly with dry ether. The ether extract is protected as much as possible from atmospheric moisture. Evaporation of the ether leaves a dark brown, tarry residue. This is distilled at 2 mm. At 60° (approx.) a colorless oil starts to come over. At 101° a yellow oil appears. The distillation is continued until the temperature reaches 120° . At this point only a high-boiling tar is left in the distilling flask. The oil collected between 60° and 120° is preserved for redistillation. Yield: 2.6 g.

No attempt to fractionate is made in this first distilla-

tion. Its purpose is merely to remove the tar, which interferes with the smooth distillation necessary for fractionating. The weight of the benzamide heated with lime never exceeds 10 grams, since the yield of oil does not increase proportionately if larger samples are used. Consequently it is best to allow the oil obtained from many decompositions, after it has been separated from the tar, to accumulate until at least 10 grams is at hand. This amount can then be fractionally distilled.

Some of the tar-free oil (9 g.) collected in this manner is fractionally distilled, in a vacuum. At 2 mm. of pressure, a colorless oil is collected between 57° and 101° ; 6 g. of straw-colored liquid comes over between 101° and 106° . This last fraction is redistilled, again at 2 mm., and the greater portion of it (4.5 g.) boils at $101-3^{\circ}$. This fraction distills very sharply and smoothly. The distilling flask is heated with a bath of mineral oil, which is kept between 110° and 120° . Lenth reported $112^{\circ}/4$ mm. as the boiling point of the oil obtained by him through heating the impure benzoyl derivative of the methylated alkamine (177°).

The $101-3^{\circ}$ fraction has an odor strongly reminiscent of pyridine, though lacking the intense, sickening quality of that compound. This fact is entirely compatible with our ideas on the structure of this oil, since, like pyridine, it is assumed to have a carbon-nitrogen ring.

The chloroplatinate of this compound, the supposed unsymmetrical diphenylethylenemethylimide, $(C_6H_5)_2C-\overbrace{CH_2-NCH_3}$, was prepared and analyzed for platinum. Half a gram of the oil is dissolved in 5 c.c. of absolute alcohol. To this solution 2 c.c. of a 10 per cent absolute alcohol solution of chloroplatinic acid is added. The bright yellow platinum salt precipitates immediately.

It is brought upon a filter, washed well with anhydrous ether, and dried over phosphorous pentoxide in a vacuum. The analysis (Pregl):

5.988 mg. of sample	gives	1.421 mg. of Pt.
5.024 mg. " " "		1.186 mg. of Pt.
4.598 mg. " " "		1.092 mg. of Pt.

<u>Calculated for</u> $(C_{15}H_{16}N)_2PtCl_6$:	<u>Found</u> :
Pt: 23.55 per cent	23.73 per cent
	23.61
	23.75

The melting point of the chloroplatinate is 191° .

Analysis (Pregl) for carbon and hydrogen of the supposed diphenylethylenemethylimide, $(C_6H_5)_2\overbrace{C-CH_2}^{NCH_3}$:

5.101 mg. of oil	gives	3.197 mg. of H_2O .
5.101 mg. " " "		16.066 mg. of CO_2 .
4.789 mg. " " "		2.974 mg. of H_2O .
4.789 mg. " " "		15.077 mg. of CO_2 .

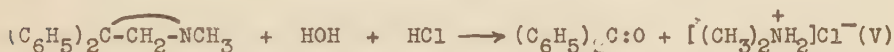
<u>Calculated for</u> $C_{15}H_{15}N$:	<u>Found</u> :
H: 7.23 per cent	7.01, 6.95 per cent
C: 86.08	85.90, 85.86

Three of the above results just fail to come within the 0.20 per cent error allowed by Pregl, but seem to agree closely enough to verify the formula assigned to the compound. Lenth was unable to get acceptable results from his carbon and hydrogen analyses of the oil. This is probably due to the fact that the benzoyl derivative from which he obtained his oil was really a mixture of the methylated and non-methylated compounds. Since it is known that heating the benzoyl derivative of the non-methylated alkamine with lime gives methyliminobenzophenone, $(C_6H_5)_2C:NCH_3$, as shown by Maver, Cole, and Lenth, Lenth must have had his oil contaminated with varying amounts of that compound. This would account for his erratic carbon and hydrogen determinations. Since methyliminobenzophenone does not form a chloroplatinate, he was able to prepare a pure platinum salt of the ring compound without interference

by the imine.

9. Acid Hydrolysis of Unsymmetrical Diphenylethylene-methylimide, $(C_6H_5)_2C-CH_2-NCH_3$.

Lenth hydrolyzed the ring compound with dilute hydrochloric acid in order to verify the structure assigned to it. He found that the products of hydrolysis were benzophenone and dimethylamine, according to the following equation:



This experiment was repeated by the author. The oil (0.5 g.) is heated for ten minutes with dilute hydrochloric acid. The cooled mixture is extracted with ether. The ether solution is evaporated to a thick, brown liquid. As a test for benzophenone the liquid is refluxed for 15 minutes with an excess of a mixture of sodium hydroxide and hydroxylamine hydrochloride solutions. When the solution has cooled, it is carefully acidified with dilute hydrochloric acid, and crystals are formed. These are recrystallized from 95 per cent alcohol, and are found to melt at 140° . They do not depress the melting point of pure benzophenone oxime (140°).

Dimethylammonium chloride is identified as the second product of the reaction by the following process:

The water extract from the hydrolysis mixture is evaporated to dryness. A crystalline residue remains. This residue is dried over phosphorus pentoxide, in a vacuum, and then dissolved in absolute alcohol. A white, crystalline compound is precipitated from the alcoholic solution by the addition of anhydrous ether. The purified product is again taken up in absolute alcohol, and then treated with an excess of a 10 per cent absolute alcohol solution of chloroplatinic acid. A bright yellow platinum salt precipitates immediately. This material is brought upon a

filter, washed well with anhydrous ether, and dried over phosphorus pentoxide, in vacuo.

Analysis for platinum (Pregl):

5.129 mg. sample gives 2.004 mg. of Pt.
5.568 mg. " " 2.181 mg. of Pt.

<u>Calculated for</u> $[(CH_3)_2\overset{+}{N}H_2]_2PtCl_6^-$:	<u>Found:</u>
Pt: 39.04 per cent	39.07 per cent 39.18

These results verify those of Lenth, and establish Equation V definitely.

10. The Thermal Decomposition of β, β -Diphenyl- β -hydroxyethylmethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$.

β, β -Diphenyl- β -hydroxyethylmethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$, 4 grams, is intimately mixed with 5 grams of freshly powdered lime, and is heated for 2 hours at 275° to 290°, in an atmosphere of dry nitrogen. The set-up of apparatus is the same as is used in heating the benzoyl derivative. When the contents of the reaction vessel have cooled, they are extracted repeatedly with anhydrous ether. The ether is removed by evaporation, and a thick, dark-brown oil remains. This is distilled under reduced pressure.

At 80-2° and 2 mm. a heavy, colorless oil is collected. It has a pleasant, pungent odor resembling that of the higher aromatic hydrocarbons. Yield: 1.2 g.

This oil does not give a test for nitrogen on decomposition with sodium, nor is it soluble in dilute hydrochloric acid. These tests indicate that it is not an amine. No reaction can be perceived when it is shaken with concentrated sulfuric acid. According to Kamm,¹ this last test shows that the material is either a saturated aliphatic hydrocarbon, an aromatic hydrocarbon, or a

¹Kamm, "Qualitative Organic Analysis," Wiley & Sons.

halogen derivative of one of these two classes of compounds. A bromine test for unsaturation proves negative. There are three hydrocarbons that might readily be formed in this reaction: unsymmetrical diphenylmethane, $(C_6H_5)_2CH_2$; unsymmetrical diphenylethane, $(C_6H_5)_2CH-CH_3$; and unsymmetrical diphenylethylene, $(C_6H_5)_2C=CH_2$.

Following are the results of carbon and hydrogen analyses:

3.333 mg. sample gives 2.332 mg. of H_2O , and
11.221 mg. of CO_2 .

4.935 mg. sample gives 3.503 mg. of H_2O , and
16.642 mg. of CO_2 .

3.699 mg. sample gives 2.667 mg. of H_2O , and
12.686 mg. of CO_2 .

<u>Calculated for:</u>		<u>Found:</u>		<u>Deviation</u> <u>from $C_{14}H_{14}$:</u>
$(C_6H_5)_2CH-CH_3$, $C_{14}H_{14}$	%H: 7.75% C: 92.25	%H: 7.83% 7.94 8.07		+0.08% +0.19 +0.32
$(C_6H_5)_2CH_2$, $C_{13}H_{12}$	H: 7.20 C: 92.80	%C: 91.82 91.97 (93.53)		-0.43 -0.28 (+1.28)
$(C_6H_5)_2C=CH_2$, $C_{14}H_{12}$	H: 6.72 C: 93.28			

It is evident that the results agree best with the formula $C_{14}H_{14}$, which is the composition of unsymmetrical diphenylethane, $(C_6H_5)_2CH-CH_3$. Aside from the qualitative and quantitative analyses described above, the compound has not been investigated further. The atmospheric boiling point cannot be determined because decomposition takes place at elevated temperatures.

SUMMARY

1. Attempts to repeat the work of Lenth on the preparation of unsymmetrical diphenylethylenemethylimide, $(C_6H_5)_2C=CH_2-NCH_3$, from β, β -diphenyl- β -hydroxyethylmethylbenz-

amide, $(C_6H_5)_2C(OH)CH_2N(CH_3)COC_6H_5$, are reported.

While the formation of this interesting derivative of an ethylenimide ring, under the conditions used by Lenth, is confirmed, it is shown that the latter's product, a basic oil, should not have been pure.

2. Before the formation of the non-methylated ring derivative, $(C_6H_5)_2C-CH_2-NH$, was attempted, a new path to the pure diphenylethylenemethylimide is developed, based on the complete separation and purification of the primary and secondary amines, β, β -diphenyl- β -hydroxyethylamine, $(C_6H_5)_2C(OH)CH_2NH_2$, and β, β -diphenyl- β -hydroxyethylmethylamine, $(C_6H_5)_2C(OH)CH_2NH(CH_3)$, and their derivatives, by way of the benzenesulfonamides.

3. The preparation and separation of β, β -diphenyl- β -hydroxyethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2NH.SO_2C_6H_5$, and β, β -diphenyl- β -hydroxyethylmethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$, are described.

4. A description of the methylation, with dimethyl sulfate, of the unmethylated benzenesulfonyl derivative, $(C_6H_5)_2C(OH)CH_2NH.SO_2C_6H_5$, is given.

5. A new method for removing acyl groups from the acyl derivatives of primary and secondary amines is developed, and applied to the production of pure β, β -diphenyl- β -hydroxyethylmethylamine, $(C_6H_5)_2C(OH)CH_2NH(CH_3)$, from its benzenesulfonyl derivative.

6. The preparation and analysis of pure β, β -diphenyl- β -hydroxyethylmethylbenzamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)COC_6H_5$, are given.

7. The thermal decomposition of pure β, β -diphenyl- β -hydroxyethylmethylbenzamide (see 5), resulting in the formation (see 1) of pure unsymmetrical diphenylethylenemethylimide,

$(C_6H_5)_2\overline{C-CH_2-NCH_3}$, is described. Analyses of this oil and its chloroplatinate are given. Lenth's carbon and hydrogen analyses of this compound were erratic, due to impurities inherent in his method of preparation; his analysis for platinum in the chloroplatinate agreed with ours, however, because of the inability of these impurities to form chloroplatinates.

8. The acid hydrolysis of the ring derivative, $(C_6H_5)_2\overline{C-CH_2-NCH_3}$, is proved to yield benzophenone and dimethylamine. This not only confirms and definitely establishes Lenth's findings, but strongly supports the view that in the molecular rearrangement of β,β -diphenyl- β -hydroxyethylamine, $(C_6H_5)_2C(OH)CH_2NH_2$, to form methyliminobenzophenone, $(C_6H_5)_2C:NCH_3$, the ring derivative, $(C_6H_5)_2\overline{C-CH_2-NH}$, is first formed, and then goes over into methyliminobenzophenone. The test of this theory of molecular rearrangement is the ultimate goal of these investigations.

9. Analysis indicates that the product of the thermal decomposition of β,β -diphenyl- β -hydroxyethylmethylbenzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$, with lime, has the empirical formula $C_{14}H_{14}$, corresponding to unsymmetrical diphenylethane, $(C_6H_5)_2CH-CH_3$.

In conclusion, the author wishes to express his gratitude to Professor Stieglitz for his inspiring guidance. He also wishes to thank Dr. R. W. Johnson and Dr. E. W. Lowe for many helpful suggestions.

